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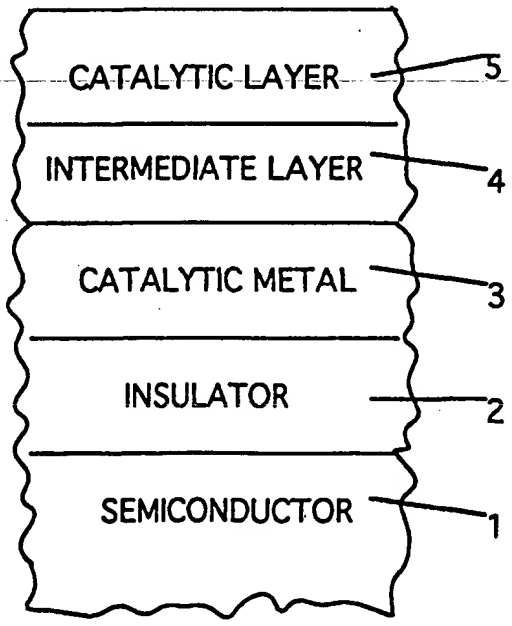
(54) Title: METHOD AND DEVICE FOR GAS SENSING

(57) Abstract

The present invention is a gas sensitive semiconductor device suitable for forming arrays having one or more elements containing at least two layers disposed on a semiconductor substrate, the layers offering better long term stability and faster response compared to elements with only one layer. The layer in contact with the gas to be detected is catalytically active while the other layers do not have to be catalytic but provide changes in the electric field outside the semiconductor in the presence of the gas to be detected. The sensing portion may be operated up to about 1000 °C and is therefore of interest for gas sensitive devices based on e.g. silicon carbide or diamond capable of operation at higher temperatures than that for silicon based devices.



METHOD AND DEVICE FOR GAS SENSING

Technical field

The present invention relates to a method and a device for gas sensing and particularly for gas sensing at high ambient temperatures.

Prior art

It is known that catalytic metals can be used as gates for gas sensitive field effect devices (transistors, capacitors, diodes, etc). Thus they comprise metal-insulator-semiconductor- or metal-semiconductor structures. Such devices may be used to measure small concentrations of molecules like hydrogen, hydrogen sulfide, alcohols, hydrocarbons, ammonia, amines, etc. The highest operation temperature is determined by the semiconductors used, which e.g. for silicon is about 250°C but for silicon carbide about 1000°C.

The gas sensitivity occurs because reaction intermediaries (like hydrogen atoms) give rise to electrical phenomena at the metal-insulator or metal-semiconductor interface, which changes the electric field outside the semiconductor.In Fig. 1 is demonstrated, in a simple cross section, a structure of prior art semiconductor sensors. A problem with this type of device is that slow phenomena occurs (structural changes in the metal and/or slow adsorption sites for the reaction intermediaries at the interface) which give rise to stability problems and slow responses (hysteresis).

In U.S. Patent Application No. 5,273,779 is described a method of fabricating a gas sensor and the product fabricated thereby. The device comprises a substrate, a buffer layer coated on the substrate, a pair of electrodes disposed on the gas sensing layer, at least one gas sensing layer arranged on the buffer layer and a catalytic layer coated on the gas sensing layer. However the device is not a field effect device but based on conductivity changes in the sensing layers. Additionally the buffer layer is used to prevent reaction between the gas sensing layer and the substrate, i.e. the buffer layer has no function in the gas detection.

In U.S. Patent Application No. 4,337,476 is described a method using silicon-rich silicides. Silicon-rich silicides of titanium and tantalum formed by sintering a cosputtered alloy with silicon to metal ratio of three are replacing polysilicon as the gate metal in semiconductor integrated circuits. The technique is used as a normal contact forming procedure in for

mono or multi layer constitute an intermediate layer in the process of detecting gas, the intermediate layer being different from the catalytic metal layer and the catalytically active layer and may also have electrical properties making it suitable as a part of the semiconductor device.

According to a third object of the present invention the catalytic layer and intermediate layer are deposited on an insulator layer, preferably an oxide, primarily deposited onto the semiconductor substrate to form a field effect structure, such as a field effect transistor, a metal-insulator-semiconductor capacitor, metal thin insulator semiconductor diode, Schottky barrier device or a tunneling device.

According to a fourth object of the invention the catalytically active material consists of catalytic metals, alloys or compounds, oxides, ceramics or polymers, and the intermediate layer is silicide, for example tantalum silicide.

According to a fifth object of the present invention the semiconductor device is fabricated using wide band-gap semiconductor material having band-gap being at least 1.5 eV, for example silicon carbide or diamond.

According to a sixth object of the present invention is provided a method of fabricating a gas sensor array comprising at least one gas sensitive semiconductor device including a suitably doped semiconductor substrate, having the steps of application by evaporation or sputtering, preferably by DC-magnetron sputtering through a mask, of a first mono or multi layer onto the substrate, which layer forms an intermediate layer, whereby this first layer together with a catalytic layer in contact with the gas to be measured is generating a change in the electric field outside the semiconductor and has electrical properties making it suitable as a part of the semiconductor device, and application in the same way of a second layer being catalytically active, consisting of catalytic metals, alloys or compounds, oxides, ceramics or polymers on top of the first layer or layers.

According to a seventh object of the present invention is provided a method of fabricating a gas sensor array comprising at least one gas sensitive semiconductor device including a suitably doped semiconductor substrate provided with a catalytic metal layer, having the steps

A description of an illustrative embodiment

1. Introduction

Chemical sensors operating at high temperatures are of interest in several types of combustion control. Furthermore for sensors based on the use of catalytic metals as active sensing elements a high temperature means that molecules like saturated hydrocarbons also can be detected. Field effect devices according to the state of the art based on silicon are limited to temperatures below about 250°C. Therefore it has been of interest to develop field effect devices having catalytic metal gates based on silicon carbide as the semiconductor. Silicon carbide, e.g. 6H-SiC, has a band-gap of about 2,9 eV. Field effect devices based on SiC can therefore be operated up to at least 800°C. A platinum-oxide-silicon carbide structure (Pt-MOSiC) can be used to detect hydrogen and (saturated) hydrocarbons at such temperatures as discussed in "Chemical sensors for high temperatures based on silicon carbide", by A. Arbab et al., Sensors and Materials, 4, 4, 1993, pp 173-185, "Gas sensors for high temperature operation based on metal oxide silicon carbide (MOSiC) devices", by A. Arbab et al., Sensors and Actuators B, 15-16, 1993, pp 19-23, and "Evaluation of gas mixtures with high-temperature gas sensors based on silicon carbide", by A. Arbab et al., Sensors and Actuators B, 18-19, 1994, pp 562-565, which hereby are refered to. Arbab was previously the name of the present inventor Baranzahi.

The high temperature operation of the sensors caused, however, also some problems related e.g. to the stability of the catalytic metal gate. A phenomenon called catalytic etching may occur during reactions between hydrogen containing molecules and oxygen on catalytic metals at temperatures above 450°C which is discussed for example by V. W. Dean et al., in J. Phys. Chem. 92, 1988, pp 5731-5738. Further more there may be changes in the structure of the catalytic metal. These phenomena can change the area of the metal contact and hence cause a long term drift of the sensor signal. Field effect devices according to the state of the art have also often slow adsorption sites for the reaction intermediary at the catalytic metal insulator interface causing drift and/or hysteresis phenomena.

Here will, however be disclosed a method to fabricate a device which shows a fast response and a good stability both during operation and storage as well as a description of the actual component intended for a gas sensing array.

structure of prior art according to Fig. 1)

Substrate of sample 2 received 0,3 nm Cr + 300 nm Pt, electron gun evaporation through a copper mask having a diameter 1,0 mm and no external heating of the substrate. (Two layer structure corresponding to the prior art sample 1)

Substrate of sample 3 received 50 nm Pt + 50 nm $TaSi_x$ + 100 nm Pt, DC-magnetron sputtered through a copper mask having a diameter of 1,0 mm with substrate temperature 350°C during sputtering. (Three layer structure of the present invention according to Fig. 2)

Fig. 2 shows a schematic picture of the structure of the sample 3 MOSiC substrate of the present invention.

The samples were then mounted on a platinum foil (contacted to ground by a platinum wire) in a small quartz cylinder placed inside a closed quartz tube about 50 cm in length and 5 cm in diameter inside a furnace, where the temperature could be varied between room temperature and 1100°C with a precision of ±4°C. The gate electrode was contacted by a platinum probe through a quartz piston inside the quartz cylinder. Gases were supplied to the samples through another quartz tube 5 mm in diameter. A computerized gas mixing system was used to mix gases in desired concentrations from a few ppm to several percent. Argon was used as the carrier gas and all gases were of 99,99 % purity or better. The total gas flow was 100 ml/min and the total pressure was about one atmosphere or slightly above.

The samples were activated by operating them at 550°C (in an atmosphere consisting of pulses of hydrogen and ethane in argon and oxygen) for 24 hours. At the activation procedure it is presumed that the composition of the Pt-$TaSi_x$ - Pt part of the structure undergoes changes. Measurements were then carried out at temperature from 350 to 700°C in steps of 25 or 50°C. Below 350°C the response time may be quite long for some molecules.

3. General experimental observations

C(V)-curves (at 650°C) for the sample 3 being the three layer gate MOSiC device are shown in Fig. 4. The curve to the right is obtained when the sensor is operated in synthetic air, 20% O_2 in Ar. The next curve to the left is due to 5000 ppm H_2 in argon. The shift of the C(V)-

concentrations of a three layer gate structure was tested. The fact that the response in oxygen at intermediate temperatures saturates at a level significantly lower than the response in argon indicates the presence of (at least) two different reaction pathways for the species causing the observed voltage shift. The voltage shift is most probably due to hydrogen atoms at the Pt-oxide interface.

The devices need an activation after fabrication as described above. The time necessary for this activation depends on the thickness of the intermediate layer. This intermediate layer undergoes changes (structural and/or compositional) during the activation.

We then have found one way of increasing the long-term stability and decreasing the time constant for the response. This is achieved by introducing an "intermediate layer" according to Figs. 2 or 3, where this layer has the following properties after the activation step:

- it lets a reaction intermediary through, and
- it stops structural degrading changes of the layers in contact with the insulator/semiconductor.

According to Fig. 3 the "intermediate layer" should also preferably:

- have electrical properties making it suitable as a part of the semiconductor device,
- give rise to electrical polarization phenomena (electric field changes) in the presence of the reaction intermediary, and
- only give rise to fast adsorption sites for the reaction intermediary (time constants $\leq$ 3 sec.).

Preferred embodiments

A first preferred embodiment of the sensing device of the present invention, shown in Fig. 3, is a two layer structure comprising a first catalytically active material 5 consisting of catalytic metals, alloys or compounds, oxides, ceramics or polymers, a second intermediate layer 4 constituted of silicide preferably a tantalum silicide, deposited on an insulator layer 2 on a semiconductor substrate 1, preferably having a wide band-gap semiconductor material, said band-gap being at least 1.5 eV. Such wide band-gap materials being for example silicon carbide or diamond. The device is preferably fabricated using the technique discussed for the

The desired properties for the intermediate layer can be achieved in different ways and with different materials, for instance it may be achieved by sandwiching different layers onto each other in order to allow the different materials to contribute with different properties. .

One can also consider the possibility of the intermediate layer being formed through interdiffusion or reaction between at least two of the sandwiched layers the outer catalytic layer combining with the layer under it to give an intermediate layer.

The intermediate layer may also be electrically insulating or conducting.

The intermediate layer also serves to protect the device from degrading structural changes. The device described here arranged in an array makes it very applicable as a combustion sensor. They are especially useful at small oxygen concentrations, where the sensitivity can be controlled by the temperature of the device. The devices according to the present invention are fast enough for such desired applications.

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said band-gap being at least 1.5 eV.

6. The gas sensing array according to claim 5, **characterized in** that said semiconductor material is silicon carbide or diamond.

7. The gas sensing array according to claim 1, 2 or 3,**characterized in** that said intermediate layer has been subjected to an annealing step, preferably heating of the device to at least 500°C

8. The gas sensing array according to claim 4, **characterized in** that said intermediate layer (4) is a silicide.

9. The gas sensing array according to claim 4, **characterized in** that said intermediate layer (4) is a tantalum silicide.

10. A method of fabricating a gas sensor array comprising at least one gas sensitive semiconductor device including a suitably doped semiconductor substrate (1), **characterized by** the steps of

application for instance by evaporation or sputtering, preferably by DC-magnetron sputtering through a mask, of a first mono or multi layer (4) onto said substrate, said first mono or multi layer forming an intermediate layer and together with a catalytic layer generating a change in the electric field outside said semiconductor and

application in the same way of a second layer (5) being catalytically active on top of said first layer or layers.

11. A method of fabricating a gas sensor array comprising at least one gas sensitive semiconductor device including a suitably doped semiconductor substrate (1) provided with a catalytic metal layer (3), **characterized by** the steps of

application by evaporation or sputtering, preferably by DC-magnetron sputtering through a mask, of a first mono or multi layer (4) onto said catalytic metal layer, where at least one of said first mono or multi layer together with catalytic layers may generate a change in the electric field outside said semiconductor, and

20. The gas sensing array according to any of the claims 1 - 9, **characterized in** said intermediate layer not being a catalytic metal.

21. The gas sensing array according to any of the claims 1 - 9, **characterized in** said intermediate layer having electrical properties making it suitable as a part of the semiconductor device,

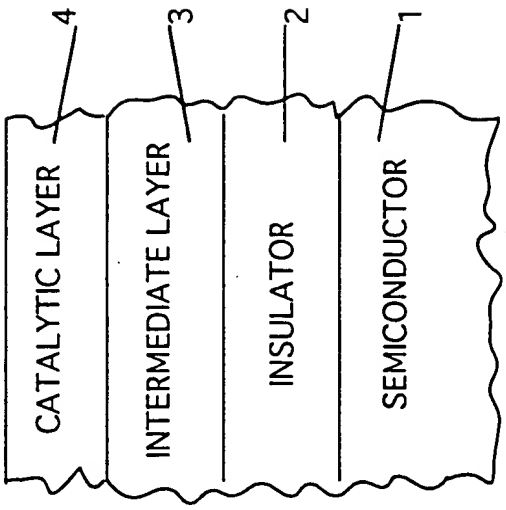

Fig. 3

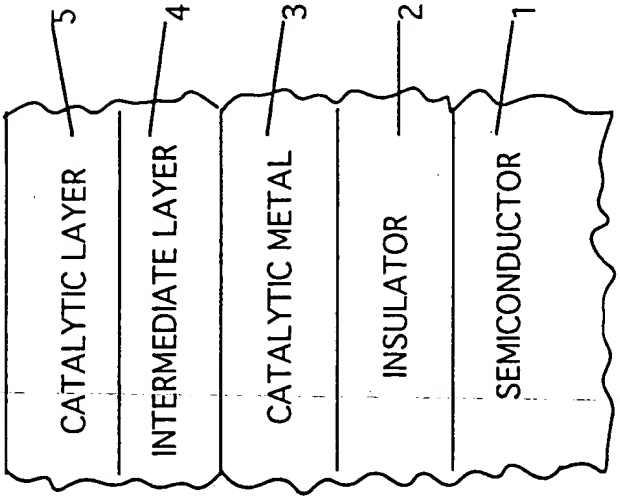

Fig. 2

PRIOR ART

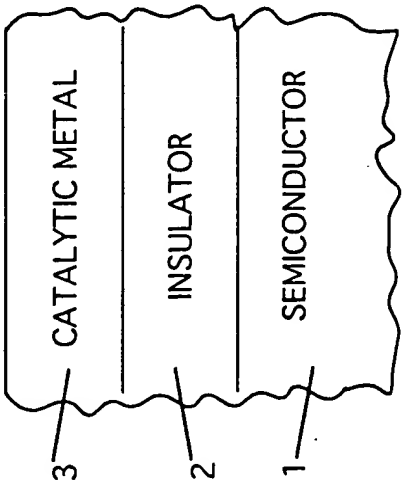

Fig. 1

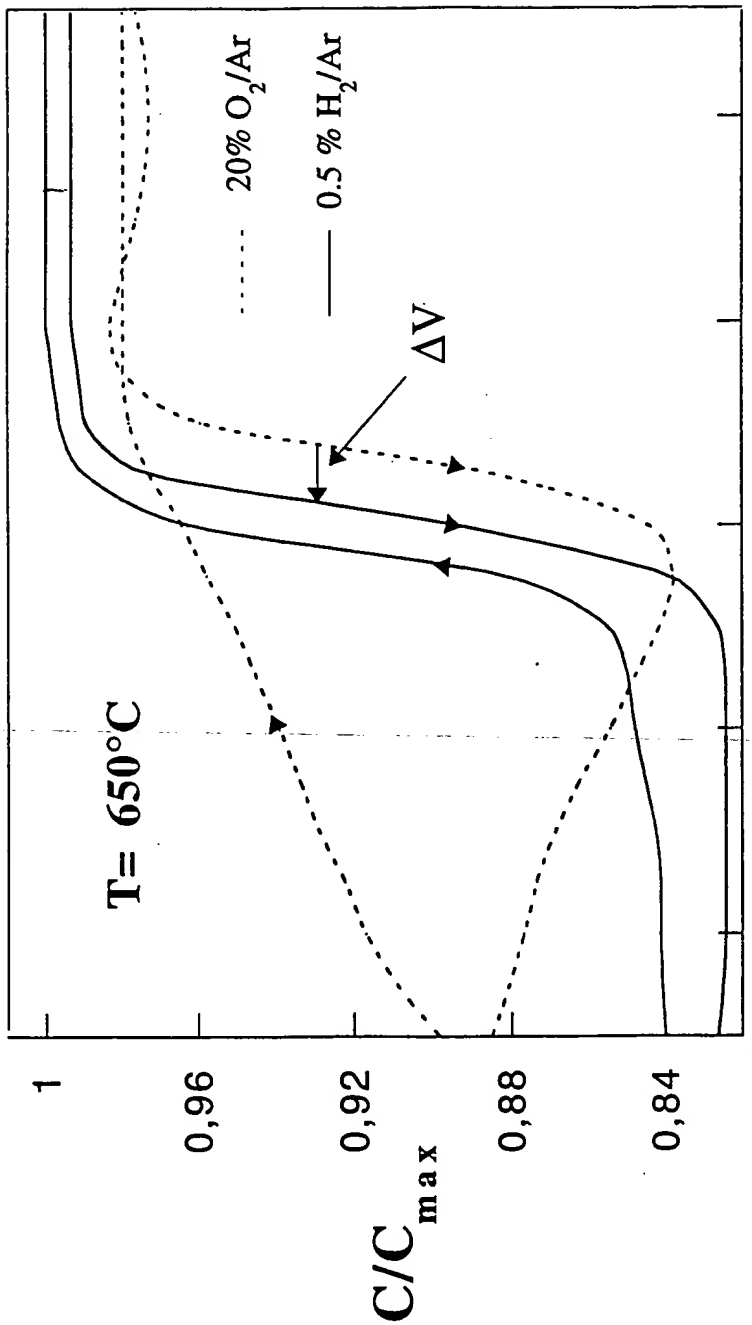
T= 650°C
20% O_2/Ar
0.5 % H_2/Ar
ΔV
C/C_{max}
1
0,96
0,92
0,88
0,84
-4
-2
0
2
4
Voltage (V)

Fig. 4

INTERNATIONAL SEARCH REPORT

Information on patent family members

05/01/96

International application No.
PCT/SE 95/01084

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A2- 0488352	03/06/92	JP-A- 5072163	23/03/93
US-A- 4875083	17/10/89	NONE	
US-A- 5285084	08/02/94	JP-A- 6222027	12/08/94
		US-A- 5362975	08/11/94
US-A- 5323022	21/06/94	AU-A- 4854693	29/03/94
		EP-A- 0659298	28/06/95
		US-A- 5409859	25/04/95
		WO-A- 9406153	17/03/94

INTERNATIONAL SEARCH REPORT

International application No.
PCT/SE 95/01084

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: G01N 27/12, G01N 27/22, H01L 29/94
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: G01N, H01L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI, EPODOC, INSPEC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0488352 A2 (MITSUI MINING COMPANY, LIMITED), 3 June 1992 (03.06.92), page 5, line 17 - page 6, line 23; page 7, line 15 - line 43 --	1-21
A	US 4875083 A (JOHN W. PALMOUR), 17 October 1989 (17.10.89), column 2, line 8 - line 17; column 3, line 42 - column 4, line 5 --	1-21
A	US 5285084 A (JESKO VON WINDHEIM ET AL), 8 February 1994 (08.02.94), column 3, line 22 - line 44; column 4, line 26 - column 5, line 38 --	1-21

[X] Further documents are listed in the continuation of Box C. [X] See patent family annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
24 January 1996	26 -01- 1996
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